

## APPENDIX A: MATRIX ELEMENTS AND EIGENVALUES

The wave functions  $\psi_1, \psi_2 \cdots \psi_n \cdots$  for the states of a quantum system are normalized and orthogonal, obeying the relations

$$\int \psi_n^* \psi_n dv = 1 \quad (1)$$

$$\int \psi_m^* \psi_n dv = 0 \quad n \neq m \quad (2)$$

In Dirac's notation  $\psi_n$  and  $\psi_n^*$  are designated  $|n\rangle$  and  $\langle n|$  while the orthogonality integrals are denoted by  $\langle m|n\rangle = \delta_{mn}$ . If  $A$  is any operator corresponding to a physical quantity the array of integrals

$$A_{mn} = \int \psi_m^* A \psi_n dv \equiv \langle m|A|n\rangle \quad (3)$$

are known as the matrix elements of  $A$  and give a matrix representation of the operator  $A$ , of the form

$$\begin{bmatrix} A_{11} & A_{12} & \cdots \\ A_{21} & A_{22} & \cdots \\ \cdots & \cdots & \cdots \end{bmatrix} \quad (4)$$

The matrix is Hermitian, i.e.,  $A_{mn} = A_{nm}^*$ . A state which satisfies the relation  $A\psi_n = a_n\psi_n$  or  $A|n\rangle = a_n|n\rangle$  is called an eigenstate of  $A$  and  $a_n$  is the corresponding eigenvalue. Eigenstates having different eigenvalues for  $A$  are always orthogonal, and if  $\psi_1, \psi_2 \dots$  are all eigenstates of  $A$  the matrix takes the diagonal form

$$\begin{bmatrix} a_1 & 0 & \cdots \\ 0 & a_2 & \cdots \\ \cdots & \cdots & \cdots \end{bmatrix} \quad (5)$$

The matrix of the operator  $AB$  is obtained from those of  $A$  and  $B$  by matrix multiplication

$$\langle l|AB|m\rangle = \sum_n \langle l|A|n\rangle \langle n|B|m\rangle \quad (6)$$

This result depends on the property that the states  $|n\rangle$  form a complete set, such that

$$\sum_n |n\rangle \langle n| = 1 \quad (7)$$

Equation (7) can be used to expand any wave function  $|\psi\rangle$  in terms of the set  $|n\rangle$

$$|\psi\rangle = \sum_n |n\rangle \langle n|\psi\rangle \quad (8)$$

In ordinary notation this reads

$$\psi = \sum_n C_n \psi_n, \quad \text{and} \quad C_n = \int \psi_n^* \psi \, dv.$$

Frequently one needs to find the eigenvalues and eigenstates of an operator, usually the energy operator  $\mathcal{H}$ , and the following procedure is used.

Consider the state  $\psi = \sum_n C_n \psi_n$ , and let  $\mathcal{H}\psi = \sum_n C'_n \psi_n$ . Then the vector  $C'_n$  is obtained from  $C_n$  as  $C'_n = \sum_m \mathcal{H}_{nm} C_m$ . Now suppose  $\mathcal{H}\psi = E\psi$ . Then it follows that

$$\sum_m \mathcal{H}_{nm} C_m = E C_n \quad (9)$$

or in matrix notation

$$\begin{bmatrix} \mathcal{H}_{11} - E & \mathcal{H}_{12} & \cdots \\ \mathcal{H}_{21} & \mathcal{H}_{22} - E & \\ \vdots & & \ddots \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ \vdots \end{bmatrix} = 0 \quad (10)$$

The allowed energy values  $E$  are the roots of the so-called *secular determinant*  $|\mathcal{H}_{mn} - E\delta_{mn}|$  of the matrix (10), while the coefficients  $C_n$ , which satisfy (10), and are correctly normalized with  $\sum_n |C_n|^2 = 1$  are the eigenvectors. The eigenvalues of a Hermitian matrix are always real. In general the matrices of two operators do not commute,  $AB \neq BA$ ; but if they do then both operators have the same eigenvectors.

## PROBLEMS

1. Verify by matrix multiplication the relations  $\sigma_x \sigma_y = i\sigma_z$  and  $\sigma_x^2 = 1$  for the Pauli spin matrices (Appendix C).
2. The matrix  $\mathbf{I} \cdot \mathbf{S}$  for two spins of 1/2 is

$$\begin{matrix} \alpha_e \alpha_n \\ \alpha_e \beta_n \\ \beta_e \alpha_n \\ \beta_e \beta_n \end{matrix} \begin{bmatrix} \frac{1}{4} & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & \frac{1}{4} \end{bmatrix}$$

Find its eigenvalues and eigenvectors.

## SUGGESTIONS FOR FURTHER READING

Landau and Lifshitz: Chapters 1 and 2.

Schiff: *Quantum Mechanics* (New York: McGraw-Hill Book Co., Inc., 1955). Chapter 6.

Eyring, Walter, and Kimball: Page 31.

Margenau and Murphy: *The Mathematics of Physics and Chemistry*, Vol. I (New York: McGraw-Hill Book Co., Inc., 1956). Chapter 10.

## APPENDIX B: TIME-INDEPENDENT PERTURBATION THEORY

The problem is to find the stationary states of a system with the Hamiltonian  $H_0 + V$ , where  $V$  is a small perturbation. The unperturbed energies and wave functions are  $E_1, E_2, \dots$  and  $\psi_1, \psi_2, \dots$  and we require the corrections to  $E_n$  and  $\psi_n$  as a series expansion in powers of  $V$ .

### 1. UNPERTURBED LEVEL NONDEGENERATE

Following Eq. (10) of Appendix A we seek solutions of the linear equations

$$\begin{bmatrix} (E_n + V_{nn} - E) & V_{nm} & \cdots \\ V_{mn} & (E_m + V_{mm} - E) & \\ \vdots & & \ddots \end{bmatrix} \begin{bmatrix} C_n \\ C_m \\ \vdots \end{bmatrix} = 0 \quad (1)$$

The zeroth approximation is  $E \doteq E_n$  and the vector  $C$  then has the form  $(1, 0, 0, \dots)$ . Next, the first-order terms from the first row of Eqs. (1) give

$$(E_n + V_{nn} - E) \cdot 1 + 0 + \cdots = 0 \quad (2)$$

and the first-order energy correction is  $V_{nn}$ . The second row, to first order in  $V$  becomes

$$V_{mn} \cdot 1 + (E_m - E_n)C_m = 0 \quad (3)$$

and yields a correction to  $C_m$ . Now substitution of the new coefficients back into the first row gives the second-order energy shift. The results then are

$$\psi = \psi_n - \sum_{n \neq m} \frac{V_{mn}}{E_m - E_n} \psi_m + \cdots \quad (4)$$

$$E = E_n + V_{nn} - \sum_{n \neq m} \frac{V_{mn}V_{nm}}{E_m - E_n} + \cdots \quad (5)$$

### 2. DOUBLY DEGENERATE LEVELS COUPLED BY V

We consider two states  $\psi_1, \psi_2$  which both have energy  $E_0$  initially. Equations (4) and (5) break down because  $(E_1 - E_2) = 0$ . Instead one must solve the matrix equations directly. Setting  $E = (E_0 + \varepsilon)$  they become

$$\begin{bmatrix} V_{11} - \varepsilon & V_{12} \\ V_{21} & V_{22} - \varepsilon \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} = 0 \quad (6)$$

The same procedure is used for any number of degenerate levels.

### 3. DOUBLY DEGENERATE LEVELS COUPLED TO HIGHER STATES

Sometimes the matrix elements of  $V$  between  $\psi_1$  and  $\psi_2$  vanish, but there are elements  $V_{1m}$ ,  $V_{2m}$  to higher states, and the equations to be solved are

$$\left[ \begin{array}{cc|ccc} (E_0 - E) & 0 & V_{1m} & \cdots & \\ 0 & (E_0 - E) & V_{2m} & \cdots & \\ \hline V_{m1} & V_{m2} & (E_m + V_{mm} - E) & & \\ \vdots & \vdots & & \ddots & \\ \vdots & \vdots & & & \ddots \end{array} \right] \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_m \\ \vdots \end{bmatrix} = 0 \quad (7)$$

The perturbed wave functions now take the form

$$\psi = C_1 \left( \psi_1 - \sum_m \frac{V_{m1}}{E_m - E_0} \psi_m \right) + C_2 \left( \psi_2 - \sum_m \frac{V_{m2}}{E_m - E_0} \psi_m \right) \quad (8)$$

while the coefficients and the energy are found by solving the matrix

$$\begin{bmatrix} U_{11} - \varepsilon & U_{12} \\ U_{21} & U_{22} - \varepsilon \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} = 0 \quad (9)$$

The elements  $U_{ik}$  ( $i, k = 1, 2$ ) are defined as

$$U_{ik} = - \sum_m \frac{V_{im} V_{mk}}{E_m - E_0} \quad (10)$$

and constitute an effective coupling between the degenerate states.

If the perturbation has both  $V_{12}$  and  $V_{1m}$  types of element one must add  $U_{ik}$  to  $V_{ik}$  and solve the combined  $2 \times 2$  matrix.

### SUGGESTIONS FOR FURTHER READING

Landau and Lifshitz: Chapter 6.

Eyring, Walter, and Kimball: Chapter 7.

## APPENDIX C: SPIN ANGULAR MOMENTUM

The same principles apply to both electron and nuclear spins. Here we shall deal with electron spin  $S$ .

The *orbital* angular momentum  $L\hbar$  of a particle is defined as  $\mathbf{r} \times \mathbf{p}$ , where  $\mathbf{p}$  is the momentum. The quantum mechanical operator for  $\mathbf{L}$  is  $-i(\mathbf{r} \times \nabla)$ , and leads immediately to the conclusion that the different components of  $\mathbf{L}$  do not commute, but  $L_x L_y - L_y L_x = iL_z$ .

The spin angular momentum  $S\hbar$  of a group of electrons obeys the same commutation rules as  $\mathbf{L}$ :

$$S_x S_y - S_y S_x = iS_z \quad (1)$$

and two others derived by rotating the  $x, y, z$  suffixes. The squared spin  $S^2 = (S_x^2 + S_y^2 + S_z^2)$  commutes with  $S_x, S_y$ , and  $S_z$ , and has the value  $S(S+1)$  where  $S$  is the total spin. The entire theory of spin follows from (1). First it is useful to introduce the shift operators

$$\begin{aligned} S^+ &= S_x + iS_y \\ S^- &= S_x - iS_y \end{aligned} \quad (2)$$

and remark that (1) leads to the important relations

$$S_z S^\pm = S^\pm (S_z \pm 1) \quad (3)$$

$$(S^2 - S_z^2) = (S^- S^+ + S_z) = (S^+ S^- - S_z) \quad (4)$$

A single electron has  $S = 1/2$ , and the two spin states  $|\alpha\rangle, |\beta\rangle$ , are eigenstates of  $S_z$  (see Appendix A) with value  $\pm 1/2$ .

$$S_z |\alpha\rangle = \frac{1}{2} |\alpha\rangle \quad S_z |\beta\rangle = -\frac{1}{2} |\beta\rangle \quad (5)$$

We shall now derive important relations for  $S^+$  and  $S^-$ .

$$\begin{aligned} S^+ |\beta\rangle &= |\alpha\rangle & S^+ |\alpha\rangle &= 0 \\ S^- |\alpha\rangle &= |\beta\rangle & S^- |\beta\rangle &= 0 \end{aligned} \quad (6)$$

The first is proved by showing that  $S^+ |\beta\rangle$  is an eigenstate of  $S_z$  with value  $+1/2$ . We use (3) and (5).

$$\begin{aligned} S_z \cdot S^+ |\beta\rangle &= S^+ \cdot (S_z + 1) |\beta\rangle = S^+ \cdot \frac{1}{2} |\beta\rangle \\ &= \frac{1}{2} \cdot S^+ |\beta\rangle \end{aligned} \quad (7)$$

This only shows that  $S^+ |\beta\rangle$  is a multiple of  $|\alpha\rangle$ . It is necessary to check that  $S^+ |\beta\rangle$  is correctly normalized. The complex conjugate state is  $\langle\beta|S^-$ , and we obtain the normalization integral  $\langle\beta|S^- S^+ |\beta\rangle$ . By (4) and (5) this reduces to  $\langle\beta|S^2 - S_z^2 - S_z |\beta\rangle = \langle\beta|S^2 + \frac{1}{4} |\beta\rangle$ . Finally it is necessary to show that

$$S^2 = \frac{3}{4} \quad (\text{spin } \frac{1}{2}) \quad (8)$$

From (5),  $S_z^2$  acting on  $|\alpha\rangle$  or  $|\beta\rangle$  simply multiplies each by  $1/4$ . Hence  $S_z^2 = 1/4$ ; by symmetry the same is true of  $S_x^2$  and  $S_y^2$ , so (8) holds. Thus we find that  $\langle\beta|S^- S^+ |\beta\rangle = \langle\beta|\beta\rangle = 1$ , and so  $S^+ |\beta\rangle$  is correctly normalized and may be identified with  $|\alpha\rangle$ .

To derive the second relation (6) we prove that the normalization  $\langle\alpha|S^- S^+ |\alpha\rangle$  of  $S^+ |\alpha\rangle$  vanishes, so the state does not exist. The matrix element is just

$$\langle\alpha|S^2 - S_z^2 - S_z |\alpha\rangle = \langle\alpha|S^2 - \frac{3}{4} |\alpha\rangle = 0$$

The matrix elements of the operators  $S_x, S_y, S_z$  are usually represented by the Pauli spin matrices  $\sigma_x, \sigma_y, \sigma_z$ , with  $S = \frac{1}{2}\sigma$ . They are

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (9)$$

The states of a general spin  $S > 1/2$  are labeled by the eigenvalue  $M_S$  or  $M$  of  $S_z$ , and written  $|S, M\rangle$  or just  $|M\rangle$

$$S_z |S, M\rangle = M |S, M\rangle \quad (10)$$

$M$  takes  $(2S+1)$  possible values  $S, (S-1) \dots -S$ . It can be shown that  $S^+$  and  $S^-$  only have matrix elements connecting  $M$  with  $(M \pm 1)$ .

$$\langle M+1 | S^+ | M \rangle = \langle M | S^- | M+1 \rangle = \sqrt{S(S+1) - M(M+1)} \quad (11)$$

Raising and lowering  $M_J$  states with *general* angular momentum  $J$  ( $J$  could be  $S$  or  $L$  or  $J$ ):

$$J_+ |M_J\rangle = \sqrt{J(J+1) - M_J(M_J+1)} |M_J+1\rangle; \quad J_- |M_J\rangle = \sqrt{J(J+1) - M_J(M_J-1)} |M_J-1\rangle$$

Two spin angular momentum vectors *which commute*, such as  $\mathbf{I}$  and  $\mathbf{S}$ , can be combined together to form a resultant

$$\mathbf{F} = \mathbf{I} + \mathbf{S} \quad (12)$$

The quantum states of the coupled system are now eigenstates of  $\mathbf{F}^2$  and  $F_z$ .  $\mathbf{F}^2$  has the value  $F(F+1)$ , while the total spin  $F$  may have one of several values. The spins  $I$  and  $S$  give a series of multiplets corresponding to the  $F$  values  $I+S, (I+S-1) \dots |I-S|$ . Each multiplet consists of  $(2F+1)$  sublevels with different  $F_z$  values. Often one needs to know the value of  $\mathbf{I} \cdot \mathbf{S}$  (nuclear hyperfine splitting) or  $\mathbf{L} \cdot \mathbf{S}$  (spin orbit splitting) in a coupled state. This is found easily:

$$\begin{aligned} \mathbf{I} \cdot \mathbf{S} &= \frac{1}{2}[(\mathbf{I} + \mathbf{S})^2 - \mathbf{I}^2 - \mathbf{S}^2] = \frac{1}{2}[\mathbf{F}^2 - \mathbf{I}^2 - \mathbf{S}^2] \\ &= \frac{1}{2}[F(F+1) - I(I+1) - S(S+1)]. \end{aligned} \quad (13)$$

The spin wave functions for two or more electrons are a little more complicated. The total spin angular momentum vector for two electrons is

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2 \quad (14)$$

and its components obey the commutation relations (1). The squared spin  $\mathbf{S}^2 = (\mathbf{S}_1 + \mathbf{S}_2)^2$  again takes the value  $S(S+1)$  but now the quantum number  $S$  may be either 0 (singlet state) or 1 (triplet state) while the resolved component  $S_z$  has the possible values 1, 0, -1. There are four possible spin wave functions

$\alpha_1\alpha_1$	$S_z = 1$
$\alpha_1\beta_2, \beta_1\alpha_2$	0
$\beta_1\beta_2$	-1

and we wish to find the wave functions of the singlet and triplet states.

The function  $\alpha_1\alpha_2$  has  $S_z = 1$  and is clearly a triplet. We check this by using Eq. (4).

$$\mathbf{S}^2\alpha_1\alpha_2 = [S^-S^+ + S_z(S_z+1)]\alpha_1\alpha_2 \quad (15)$$

But  $S^+\alpha_1\alpha_2 = (S_1^+ + S_2^+)\alpha_1\alpha_2 = 0$ , and so we find

$$\mathbf{S}^2\alpha_1\alpha_2 = S_z(S_z+1)\alpha_1\alpha_2 = S(S+1)\alpha_1\alpha_2 \quad (16)$$

To find a triplet wave function with  $S_z = 0$  we use (11) and apply the operator  $(1/\sqrt{2})S^-$ .

$$\frac{1}{\sqrt{2}}S^-\alpha_1\alpha_2 = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \quad (17)$$

A further shift down gives  $\beta_1\beta_2$  to complete the set. The only remaining spin function must be a singlet state  $(1/\sqrt{2})(\alpha_1\beta_2 - \beta_1\alpha_2)$ , since it has  $S_z = 0$  and  $\mathbf{S}^2 = 0$ . To verify this we use (4) again

$$\mathbf{S}^2(\alpha_1\beta_2 - \beta_1\alpha_2) = S^-S^+(\alpha_1\beta_2 - \beta_1\alpha_2) \quad (18)$$

$$S^+(\alpha_1\beta_2 - \beta_1\alpha_2) = (\alpha_1\alpha_2 - \alpha_1\alpha_2) = 0 \quad (19)$$

Similar methods can be used to obtain spin functions for three electrons (or nuclei) which are listed in Section 4.4.4.

## PROBLEMS

1. Construct the matrices  $S_x$ ,  $S_y$ ,  $S_z$  for spins  $S = 1$ ,  $S = 3/2$ , and  $S = 2$ .
2. Find the eigenfunctions of  $S_x$  and  $S_y$  for a spin  $S = 1$ .
3. A magnetic field  $H$  makes an angle  $\theta$  with the  $z$  axis. Find the stationary states for an electron spin  $S = 1/2$ . Calculate the probabilities that the electron will be found in the states  $|\alpha\rangle$  or  $|\beta\rangle$ .
4. A sodium atom ( $I = 3/2$ ,  $S = 1/2$ ) in zero field has the Hamiltonian  $\mathcal{H} = a\mathbf{I} \cdot \mathbf{S}$ . Find the energy levels.

## SUGGESTIONS FOR FURTHER READING

Landau and Lifshitz: Chapter 4.

Eyring, Walter, and Kimball: Chapter 9.

## APPENDIX D: TENSORS AND VECTORS

The type of tensor we are concerned with in this book is called a Cartesian tensor. Just as a vector

$$\mathbf{S} = S_x \mathbf{i} + S_y \mathbf{j} + S_z \mathbf{k} \quad (1)$$

has various components  $S_x$ ,  $S_y$ ,  $S_z$  which are referred to a set of rectangular axes  $\mathbf{i}$ ,  $\mathbf{j}$ ,  $\mathbf{k}$ , so does a Cartesian tensor. But a tensor  $\mathbf{T}$  has 9 components

$$\mathbf{T} = \begin{bmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{bmatrix} \quad (2)$$

which can be arranged to form a  $3 \times 3$  matrix. By multiplying the matrix of  $\mathbf{T}$  on the left with a row vector  $\mathbf{S}$  one obtains a new row vector  $\mathbf{S} \cdot \mathbf{T}$ . Similarly matrix multiplication on the right by a column vector  $\mathbf{I}$  yields a new column vector  $\mathbf{T} \cdot \mathbf{I}$ . Finally it is possible to form a scalar  $\mathbf{S} \cdot \mathbf{T} \cdot \mathbf{I}$  by the matrix multiplication

$$[S_x, S_y, S_z] \begin{bmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{bmatrix} \begin{bmatrix} I_x \\ I_y \\ I_z \end{bmatrix} \quad (3)$$

Note that  $\mathbf{S} \cdot \mathbf{T} \cdot \mathbf{I}$  may also be regarded as the scalar product of two vectors; either  $(\mathbf{S} \cdot \mathbf{T})$  with  $\mathbf{I}$ , or equally  $\mathbf{S}$  with  $(\mathbf{T} \cdot \mathbf{I})$ . In any case the product written in full is

$$S_x T_{xx} I_x + S_x T_{xy} I_y + \cdots S_y T_{yz} I_z + S_z T_{zz} I_z \quad (4)$$

or

$$\sum_{i,k} S_i T_{ik} I_k \quad (i, k = x, y, z) \quad (5)$$

By analogy with Eq. (1) one sometimes uses the notation

$$\mathbf{T} = \mathbf{i} T_{xx} \mathbf{i} + \mathbf{i} T_{xy} \mathbf{j} + \cdots \mathbf{k} T_{zz} \mathbf{k} \quad (6)$$



and then the scalar products  $\mathbf{i} \cdot \mathbf{T} \cdot \mathbf{i}$ ,  $\mathbf{i} \cdot \mathbf{T} \cdot \mathbf{j}$  and so on are just the components of the tensor. For example, it follows from the orthogonality of the unit vectors  $\mathbf{i}$ ,  $\mathbf{j}$ ,  $\mathbf{k}$  that

$$\mathbf{i} \cdot \mathbf{T} \cdot \mathbf{j} = (\mathbf{i} \cdot \mathbf{i})T_{xx}(\mathbf{i} \cdot \mathbf{j}) + (\mathbf{i} \cdot \mathbf{i})T_{xy}(\mathbf{j} \cdot \mathbf{j}) + \cdots (\mathbf{i} \cdot \mathbf{k})T_{zz}(\mathbf{k} \cdot \mathbf{j}) \quad (7)$$

$$= 0 + T_{xy} + \cdots 0$$

$$= T_{xy} \quad (8)$$

There are various important types of tensor. *Symmetric tensors* have a symmetric matrix;  $T_{xy} = T_{yx}$  etc. *Antisymmetric tensors* have  $T_{xy} = -T_{yx}$  and zeros on the diagonal. *Diagonal tensors*, as the name suggests, have the form

$$\begin{bmatrix} t_1 & 0 & 0 \\ 0 & t_2 & 0 \\ 0 & 0 & t_3 \end{bmatrix} \quad (9)$$

$t_1, t_2, t_3$  are called the principal values of the tensor, and if  $\mathbf{T}$  is diagonal in a certain rectangular coordinate system, the coordinate axes are known as the principal axes.

The diagonal sum of a tensor is an important quantity called the *trace* of the tensor denoted by the symbol  $\text{Tr}\{ \}$ .

$$\text{Tr}\{\mathbf{T}\} = (T_{xx} + T_{yy} + T_{zz}) \quad (10)$$

Finally a most useful tensor is the unit tensor  $\mathbf{1}$ , or  $(\mathbf{ii} + \mathbf{jj} + \mathbf{kk})$  whose matrix is the unit matrix

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (11)$$

The main reason for using tensor notation is that it is extremely easy to change from one set of rectangular axes to another. The orientation of an axis system  $\alpha, \beta, \gamma$  with respect to another set  $x, y, z$  is specified by 9 direction cosines  $l_{\alpha x}, l_{\beta x}, \dots$  which form a matrix

$$\mathbf{L} = \begin{bmatrix} l_{\alpha x} & l_{\beta x} & l_{\gamma x} \\ l_{\alpha y} & l_{\beta y} & l_{\gamma y} \\ l_{\alpha z} & l_{\beta z} & l_{\gamma z} \end{bmatrix} \quad (12)$$

Each component is the scalar product of one of the unit vectors  $\mathbf{i}, \mathbf{j}, \mathbf{k}$  with one of the new unit vectors  $\mathbf{a}, \mathbf{b}, \mathbf{c}$ ;  $l_{\alpha z}$  for instance is equal to  $(\mathbf{a} \cdot \mathbf{k})$ , and is the same as  $l_{z\alpha}$ . The rows (or columns) of (12) form a set of orthogonal normalized vectors.

To calculate the components of vectors and tensors in the new coordinate system we first note that

$$\begin{aligned} \mathbf{a} &= (\mathbf{a} \cdot \mathbf{i})\mathbf{i} + (\mathbf{a} \cdot \mathbf{j})\mathbf{j} + (\mathbf{a} \cdot \mathbf{k})\mathbf{k} \\ &= l_{\alpha x}\mathbf{i} + l_{\alpha y}\mathbf{j} + l_{\alpha z}\mathbf{k} \end{aligned} \quad (13)$$

Hence the  $\alpha$  component of a vector  $\mathbf{S}$  is

$$S_\alpha = (\mathbf{S} \cdot \mathbf{a}) = l_{\alpha x}S_x + l_{\alpha y}S_y + l_{\alpha z}S_z \quad (14)$$

Similarly the  $\alpha\beta$  component of a tensor  $\mathbf{T}$  becomes

$$\begin{aligned} T_{\alpha\beta} &= \mathbf{a} \cdot \mathbf{T} \cdot \mathbf{b} \\ &= (l_{\alpha x}\mathbf{i} + l_{\alpha y}\mathbf{j} + l_{\alpha z}\mathbf{k}) \cdot \mathbf{T} \cdot (l_{\beta x}\mathbf{i} + l_{\beta y}\mathbf{j} + l_{\beta z}\mathbf{k}) \\ &= l_{\alpha x}T_{xx}l_{\beta x} + l_{\alpha x}T_{xy}l_{\beta y} + \cdots \end{aligned} \quad (15)$$



The new matrix of  $\mathbf{T}$  can be written as the product of (2) with  $\mathbf{L}$  and its transpose:

$$\begin{bmatrix} l_{\alpha x} & l_{\beta x} & l_{\gamma x} \\ l_{\alpha y} & l_{\beta y} & l_{\gamma y} \\ l_{\alpha z} & l_{\beta z} & l_{\gamma z} \end{bmatrix} \begin{bmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{bmatrix} \begin{bmatrix} l_{x\alpha} & l_{x\beta} & l_{x\gamma} \\ l_{y\alpha} & l_{y\beta} & l_{y\gamma} \\ l_{z\alpha} & l_{z\beta} & l_{z\gamma} \end{bmatrix} \quad (16)$$

The transformation (16) has two important properties. First it follows from the orthogonality of the direction cosines that the trace of  $\mathbf{T}$  is unchanged.

$$(T_{\alpha\alpha} + T_{\beta\beta} + T_{\gamma\gamma}) = (T_{xx} + T_{yy} + T_{zz}) \quad (17)$$

Second, if the tensor is *real* and *symmetric* it is always possible to find a new axis system for which  $\alpha, \beta, \gamma$  are principal axes and the tensor is diagonal. The procedure for finding principal axes is identical with the procedure which was described in Appendix A for finding the eigenvectors of an operator. For instance, to find the direction of the  $\alpha$  axis and the corresponding principal value  $t_1$  we look for solutions of the equations

$$\begin{bmatrix} (T_{xx} - t_1) & T_{xy} & T_{xz} \\ T_{yx} & (T_{yy} - t_1) & T_{yz} \\ T_{zx} & T_{zy} & (T_{zz} - t_1) \end{bmatrix} \begin{bmatrix} l_{x\alpha} \\ l_{y\alpha} \\ l_{z\alpha} \end{bmatrix} = 0 \quad (18)$$

In connection with these transformations it is noteworthy that the scalar quantity  $\mathbf{S} \cdot \mathbf{T} \cdot \mathbf{I}$  is invariant, and so is the unit tensor (11). Conversely the only tensor which is invariant under all rotations of axes is the unit tensor  $\mathbf{1}$ , or a multiple of it.

Finally let us consider the average behavior relative to space axes  $x, y, z$  of a tensor which belongs to a rapidly rotating molecule in solution. In the molecular axis system  $\alpha\beta\gamma$  the components  $T_{\alpha\alpha}, T_{\alpha\beta}$  etc. are fixed, but the space values  $T_{xx}, T_{xy}, \dots$  fluctuate in a random manner. The time average of  $\mathbf{T}$  is an invariant tensor, so it must be a multiple of  $\mathbf{1}$ . Also the trace of  $\mathbf{T}$  is invariant, so the time average consists of a diagonal tensor with

$$t_1 = t_2 = t_3 = \frac{1}{3}(T_{xx} + T_{yy} + T_{zz}) \quad (19)$$

Clearly a tensor with zero trace vanishes on the average.

## PROBLEMS

1. Write out the vectors  $\mathbf{S} \cdot \mathbf{T}$  and  $\mathbf{T} \cdot \mathbf{I}$  in matrix notation.
2. When, if ever, is  $\mathbf{S} \cdot \mathbf{T} \cdot \mathbf{I}$  equal to  $\mathbf{I} \cdot \mathbf{T} \cdot \mathbf{S}$ ?
3. Write out in full the orthogonality conditions for the rows and columns of (12). Hence prove (17).
4. The tensor  $\mathbf{T}$  is diagonal in the axis system  $x, y, z$ . The unit vectors  $\mathbf{a}, \mathbf{b}, \mathbf{c}$  are obtained by rotating the  $\mathbf{i}, \mathbf{j}, \mathbf{k}$  axes through an angle  $\theta$  in the  $xy$  plane. Find the components of  $\mathbf{T}$  in the  $\alpha, \beta, \gamma$  system.
5. Do Problem 4 again, interchanging the axis systems.
6. The e.s.r. spectrum of the  $\text{CH}(\text{COOH})_2$  radical was studied in a single crystal to determine the hyperfine tensor of the CH proton. The components (in Mc/s) referred to crystal axes are

$$\begin{bmatrix} -53 & -7 & -17 \\ -7 & -82 & -15 \\ -17 & -15 & -41 \end{bmatrix}$$

Find the principal values and the principal directions.

7. The  $g$  tensor of the  $\text{CH}_2(\text{COOH})$  radical in the same crystal as Problem 6 is

$$\begin{bmatrix} 2.0033 & -0.0005 & 0.0000 \\ -0.0005 & 2.0028 & 0.0010 \\ 0.0000 & 0.0010 & 2.0033 \end{bmatrix}$$

Find its principal values. Are the principal directions the same as in Problem 6? Comment on the result.

### SUGGESTIONS FOR FURTHER READING

Morse and Feshbach: *Methods of Theoretical Physics*, Part I. (New York: McGraw-Hill Book Co., Inc., 1953.) Pages 54–107.